

Effect of Mixed Monomers on the Synthesis of Ion-Exchange Membranes by Radiation-Induced Grafting

HIDEKI OMICHI and JIRO OKAMOTO, *Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma 370-12, Japan*

Synopsis

Ion-exchange membranes were synthesized by radiation-induced grafting of methyl- α,β,β -trifluoroacrylate (MTFA) and also by cograftering of MTFA with propylene. Although a larger grafting yield was obtained by cograftering, the number of repeating units introduced in a unit volume of the graft films was unchanged. The electrical conductivity of the cograftered polymer film was higher than that of the film grafted with MTFA alone when compared at the same number of repeating units. This result was well correlated with the difference in distribution of graft chains in polymer films observed by ESCA and EPMA. The more homogeneous the distribution was, the higher the electrical conductivity. It was suggested that an alternating copolymerization of MTFA with propylene was responsible for the homogeneous distribution of graft chains obtained by cograftering.

INTRODUCTION

As radiation-induced graft polymerization is a convenient means of introducing functional groups into polymers, it has been applied to the production of ion-exchange membranes. In particular, grafting of acrylic acid on polyethylene (PE), polytetrafluoroethylene (PTFE) films, etc., has been intensively studied.¹⁻⁴

Recently, ion-exchange membranes have been used for electrolysis of brine and pure water. The membranes should be durable when contacted with chlorine, oxygen, and alkaline solution at high temperature. Only perfluoropolymer membranes are considered desirable.^{5,6} The membrane obtained by grafting of acrylic acid mentioned above was, on the other hand, found less suitable to be used for this purpose.⁷

In our previous works⁷⁻⁹ grafting of a fluorine-containing monomer was attempted to make membranes durable under such severe conditions. At first methyl- α,β,β -trifluoroacrylate (MTFA) was grafted, and the grafted films were hydrolyzed. These films, however, showed small electrical conductivity not sufficient to be used as membrane. Then, MTFA was mixed with other monomers such as olefinic monomers and cograftering was attempted. Finally, a highly conductive polymer membrane was obtained by cograftering of MTFA with propylene (Pr).

The present article intends to show how the electric properties and morphological characteristics of the membrane are changed by cograftering of MTFA mixed with propylene.

EXPERIMENTAL

Films of PE (Mitsui Petrochem., HIZEX) and PTFE (Nitto Denko) 100 μm thick were used as trunk polymers for grafting. Before the reaction films were rinsed with acetone and dried in a vacuum oven for 16 h at room temperature. The synthesis of MFTA monomer and the grafting procedure were reported previously. In the case of cografting, an equimolar mixture of MFTA and Pr was used.⁷⁻⁹ A simultaneous grafting *in vacuo* was performed using ⁶⁰Co γ -rays. The electric resistance of graft films hydrolyzed in a 2N NaOH methanol/water 3:1 solution for 16 h was measured by means of the apparatus reported previously.⁷ Electron spectroscopy for chemical analysis (ESCA) spectra were measured by means of a Perkin-Elmer ESCA System, Model PHI-560. The distribution of carboxyl functional groups of the graft chains in the direction of film thickness was measured from the line profiles of potassium combined with carboxyl groups after the hydrolysis of graft films in KOH solution. A JEOL Electron-Probe X-Ray Microanalyzer, Model JXA-733, was used for the measurement. The specimens were made by cutting the films in liquid nitrogen.

RESULTS AND DISCUSSION

Graft Polymerization

Figure 1(a) shows the comparison of grafting yield of MFTA alone and that of cografting of MFTA with Pr on PE films obtained from the percentage increase in weight after separating homopolymer. A rubberlike

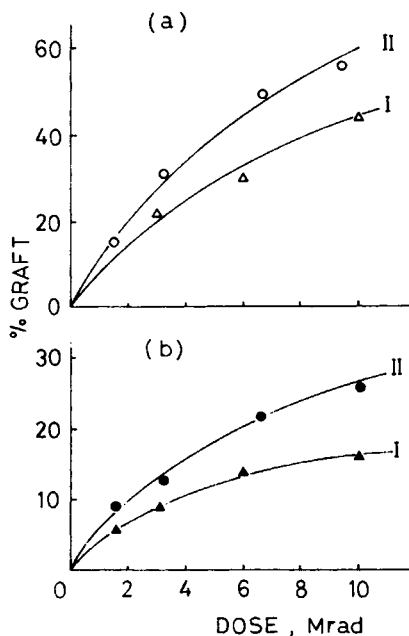


Fig. 1. The grafting yield obtained (I) by grafting of MFTA and (II) grafting of mixed monomers composed of MFTA and Pr: (a) on PE films; (b) on PTFE films. Dose rate: 1.0×10^6 rad/h, temperature: $r.t.$

copolymeric homopolymer was produced in the case of cografting. Apparently, the grafting yield of the latter is larger than that of the former. When the irradiation dose is high, the difference in grafting yield becomes more remarkable. Although the absolute grafting yield is small, a similar behavior was observed for PTFE as shown in Figure 1(b). These differences in grafting yield between cografting of MTFA with Pr and grafting of MTFA alone could be explained as follows:

The grafting yield is related to the product of the average molecular weight of graft chains and its number. The number of graft chains is based on the probability of initiation which proceeds through the contact of trunk polymer radicals with monomer. In the case of grafting MTFA alone, MTFA contacts with polymer radicals. In the case of cografting also, the initiation is due to the contact of polymer radicals with MTFA because Pr does not initiate grafting in this low pressure condition (ca. 7 kg/cm²). Therefore, it is probable that there is virtually no difference in the probability of initiation between the two graftings and the difference in the grafting yield is only due to the difference in the molecular weight of the graft chains.

It has been reported that the copolymerization of MTFA and Pr gives a copolymer with an alternate arrangement.¹⁰ This is due to the fact that MTFA has an electron-accepting character ($e = 2.37$) while Pr has an electron-donating character ($e = -0.78$), which brings about a very small value of the product of monomer reactivity ratios ($r_1 \cdot r_2 = 5 \times 10^{-5}$). Actually, the homopolymer obtained in cografting was an alternating copolymer. Referring to the report that the monomer reactivity ratios for graft polymerization with mixed monomers are approximately equal to the corresponding values for the usual copolymerization,¹¹ it is not ridiculous to assume that the present cografting of MTFA with Pr also gives an alternate copolymer graft chains. In other words, it is supposed reasonable to assume that the repeating unit of the graft chain is composed of MTFA-Pr in cografting of these monomers.

The concentration of the repeating unit per unit volume of graft polymer (n/V) can be calculated from the grafting yield G as follows:

$$\frac{n}{V} = \frac{10 \cdot G \cdot \rho}{MW} \quad (\text{mol/L}) \quad (1)$$

where ρ and MW denote the density of the polymer (g/cc) and the molecular weight of the repeating unit (140.08 for MTFA and 182.16 for MTFA-Pr), respectively.

Figure 2 shows the comparison of n/V obtained by grafting of MTFA with that of cografting of MTFA-Pr. Although the calculated values are rather scattered, n/V for grafting of MTFA is approximately equal to that for cografting both in the case of grafted PE film and grafted PTFE film. These results indicate that, for each system, swelling of film in MTFA is similar to that in MTFA/Pr. When considered with the point that the molecular weight of the graft chain is the product of the molecular weight of the repeating unit and its number, it is reasonable to conclude that the larger grafting yield obtained by cografting of MTFA-Pr is due to the larger molecular weight of the repeating unit MTFA-Pr when compared with that of MTFA.

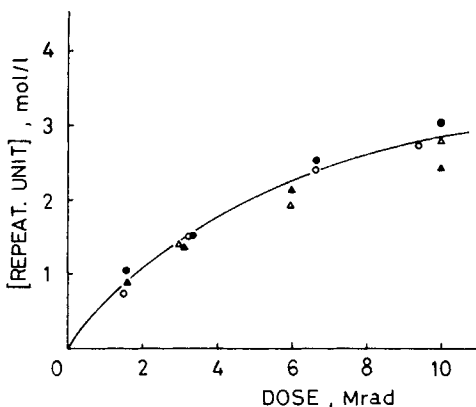


Fig. 2. The volumetric number of repeating units introduced in graft films obtained by grafting of MTFA and grafting of mixed monomers: MTFA: (Δ) PE, (\blacktriangle) PTFE; MTFA-Pr: (\circ) PE, (\bullet) PTFE.

Figure 2 also shows that n/V for PE film is roughly equal to that for PTFE film. It looks as if grafting were independent of the trunk polymer. However, as shown in our previous paper,¹² each step of grafting, propagation, and termination, in particular, is influenced by trunk polymer. Therefore, it seems that the number of repeating unit introduced to PTFE happens to be equal to that introduced to PE.

Conductivity of Grafted Films

When a certain amount of ester groups of MTFA graft chains are hydrolyzed with alkaline solution the grafted films become conductive. Figure 3 shows the relationship between the volumetric concentration n/V of carboxyl groups and the electric resistance R of the grafted films observed in 2*N* NaOH solution at 20°C. The minimum volumetric concentration of carboxyl groups necessary to provide electrical conductivity to grafted films was found ca. 1 mol/L for the polymer grafted with MTFA alone, P-*g*-MTFA, and ca. 0.5 mol/L for the polymer cogenerated, P-*g*-(MTFA-Pr), respectively.

As shown in this figure, two straight lines of almost equal slope—one for P-*g*-MTFA and the other for P-*g*-(MTFA-Pr)—can represent all the data obtained for grafted PE films and grafted PTFE films. From the slopes of these straight lines it was found that R decreases in proportion to the 2.7 power of n/V .

The result that the resistance value of P-*g*-(MTFA-Pr) is much smaller than that of P-*g*-MTFA at the same n/V value indicates the superiority of cogenerated over grafting one monomer to obtain a low electric resistance film with a small concentration of functional repeating unit.

Figure 3 also shows that the values of electric resistance of grafted PTFE film are located on the same line as those for grafted PE film. This result indicates that the conductivity of grafted films is not influenced by the trunk polymer but by the concentration of functional groups introduced in these polymer films.

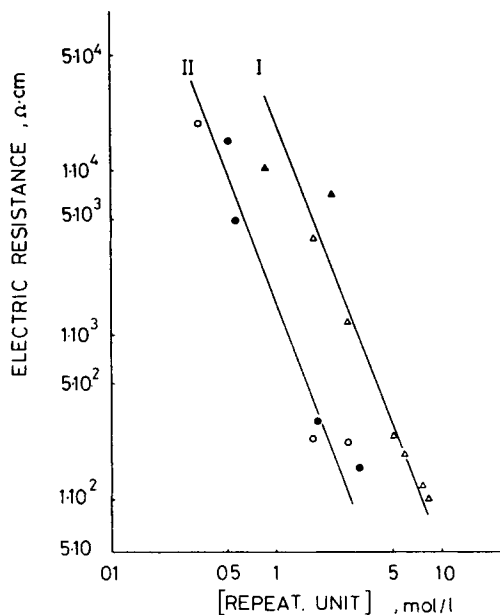


Fig. 3. Relationship between electric resistance of graft films and the number of repeating units for: (I) P-g-MTFA and (II) P-g-(MTFA-Pr). Measurement: in 2*N* NaOH solution at 20°C. 1000 Hz AC was used. The symbols are the same as shown in Figure 2.

ESCA Spectra

As shown in our previous papers,⁷⁻⁹ the conductivity of the grafted films is controlled by the distribution of functional groups in the films. The results in Figure 3 indicate that the functional groups in P-g-(MTFA-Pr) film are more appropriately distributed in the film for electric conductivity than those in P-g-MTFA film. In order to clarify this point, the composition of the surface layer of the grafted PTFE films was investigated by means of ESCA. The concentrations of the repeating unit per unit volume of the films are 1.7 mol/L for PTFE-g-MTFA film and 1.8 mol/L for PTFE-g-(MTFA-Pr) film, respectively. The films were hydrolyzed in advance with KOH solution to diminish the effect of ester groups of MTFA parts on C_{1s} spectra.

Figure 4 shows ESCA spectra of C_{1s}, F_{1s}, and O_{1s} of the grafted PTFE films. The peak of C_{1s} of PTFE-g-MTFA at ca. 292 eV is due to —CF₂— bonds of the polymer structure. A small peak at ca. 285 eV is probably due to the residual ester groups of MTFA graft chains not hydrolyzed by KOH. In the case of PTFE-g-(MTFA-Pr) a large peak due to —CH₂— bonds in Pr parts the height of which is almost comparable to that of C_{1s} due to —CF₂— bonds is observed at 285 eV.

F_{1s} appears at ca. 690 eV. This is due to both —CF₂—CF₂—structure of the trunk polymer and —CF₂—CFX— (X = COOK) structure of the graft chains. The peak of O_{1s} at 534 eV due to carboxyl groups of the graft chains is not clearly observed in PTFE-g-MTFA when compared with PTFE-g-(MTFA-Pr).

Based on the ESCA spectra the composition of the surface layer was calculated. The results are shown in Table I. The contents of C and F in

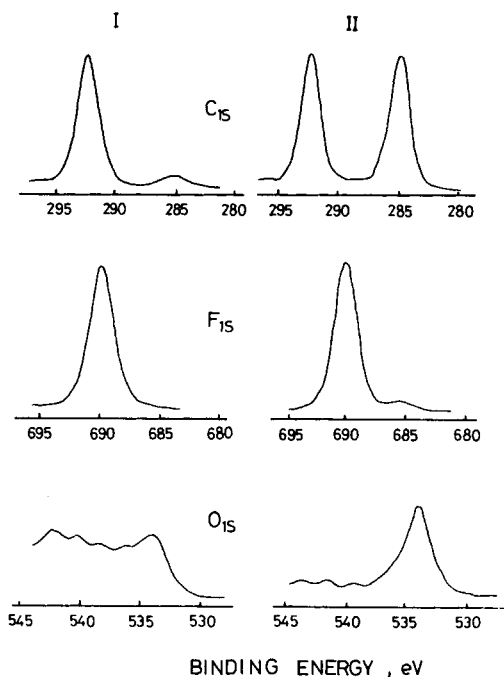


Fig. 4. ESCA spectra of (I) PTFE-*g*-MTFA and (II) PTFE-*g*-(MTFA-Pr).

PTFE-*g*-MTFA are comparable to the corresponding values in PTFE-*g*-(MTFE-Pr). On the other hand, the content of O in PTFE-*g*-(MTFE-Pr) is larger than that of PTFE-*g*-MTFA in spite of the fact that approximately equal amount of carboxyl groups (1.7–1.8 mol/L) are introduced in these grafted films, P-*g*-MTFA and P-*g*-(MTFA-Pr).

EPMA Measurement

In order to obtain a conductive film, the carboxyl groups should be distributed inside the film as well as the film surface.⁷⁻⁹ Therefore, the distribution of graft chains in the direction of film thickness observed by means of EPMA was compared between P-*g*-MTFA and P-*g*-(MTFA-Pr). Figure 5 shows line profiles of potassium combined with carboxyl groups in MTFA graft chains. When the concentration of carboxyl groups is small, two peaks exist near the film surfaces. With the increase in the concentration the area under the distribution curve increases and the peak position advances

TABLE I
Contents of Elements in the Thin Layer of Grafted PTFE Film

Element	PTFE- <i>g</i> - MTFA (%)	PTFE- <i>g</i> - (MTFA-Pr) (%)
C	35.7	36.5
F	63.0	58.8
O	1.3	4.7

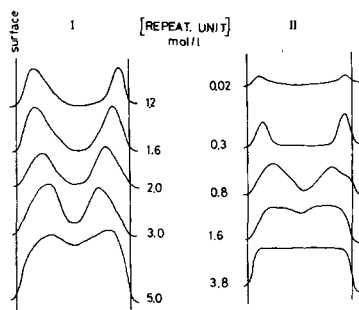


Fig. 5. Line profiles of potassium combined with carboxyl groups of graft chains: (I) *P-g*-MTFA; (II) *P-g*-(MTFA-Pr).

from the surface to the center of the film until a flat distribution curve is obtained. In the case of *P-g*-(MTFA-Pr) the distribution curve is virtually flat when the amount of functional groups in the film is about 1.6 mol/L. On the other hand, *P-g*-MTFA containing a similar amount of functional groups still has a bimodal distribution curve, which indicates that there still remains a part containing no carboxyl groups at the center of the *P-g*-MTFA film at this concentration of carboxyl groups.

In order to make this comparison of the distribution curve of carboxyl groups more quantitative, the distance of the peak from the film surface was plotted against the concentration of functional groups (repeating units). Figure 6 shows the results. There are two linear relationship curves. The slope of the straight line for *P-g*-(MTFA-Pr) is about three times that for *P-g*-MTFA. This result indicates that the layer containing carboxyl groups in *P-g*-(MTFA-Pr) film is more homogeneous than that in *P-g*-MTFA film at the same amount of carboxyl groups. One of the reasons may be the graft chain structure. As hydrolyzed MTFA homopolymer and MTFA-Pr copolymer are strong acids ($\text{pK}_a = 2-3$),¹⁰ the polymer chains are supposed to be extended like rods because of the repulsion among acid groups. Therefore, the longer graft chains of *P-g*-(MTFA-Pr) extend more inwards than the shorter graft chains of *P-g*-MTFA.

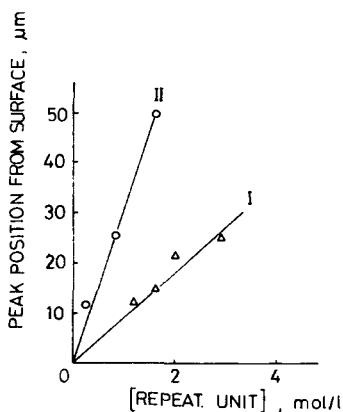


Fig. 6. Peak position in distribution curves for carboxyl groups of graft chains: (I) *P-g*-MTFA; (II) *P-g*-(MTFA-Pr).

In connection with this strong acidity, it may be pointed out that P-g-MTFA is insufficiently hydrolyzed. As shown in Figure 4 and in Table I the concentration of hydrolyzed ester groups near the film surface of P-g-MTFA is very small when compared with that of P-g-(MTFA-Pr). This result indicates the difficulty of converting ester groups to acid functional groups in P-g-MTFA. Probably, once an ester group is hydrolyzed, the strong acidity in the carboxyl group makes it difficult of further hydrolysis of adjacent ester groups in P-g-MTFA. This is due to the shorter distance between the carboxyl group and unhydrolyzed ester groups in P-g-MTFA. On the other hand, the distance is longer in P-g-(MTFA-Pr) because of the alternate arrangement of MTFA and Pr.

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